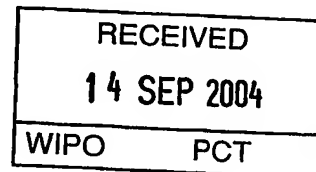


08.07.04

**Europäisches  
Patentamt****European  
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Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

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**Patentanmeldung Nr. Patent application No. Demande de brevet n°**

03077152.1

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:  
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.  
If no title is shown please refer to the description.  
Si aucun titre n'est indiqué se référer à la description.)

Optically active carbon-substituted methyl amine derivatives and their use as a  
rheology control agent

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)  
revendiquée(s)

Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

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PT RO SE SI SK TR LI

ANR 3011 PD EP

**OPTICALLY ACTIVE CARBON-SUBSTITUTED METHYL AMINE DERIVATIVES  
AND THEIR USE AS A RHEOLOGY CONTROL AGENT.**

5

The invention relates to carbon-substituted methyl amine derivatives and their use to control the rheology of compositions comprising them. Preferably the amine derivatives are used as sag control agents in coating compositions. The use of sag control agents in coating compositions is well-known. For example, US 4,311,622  
10 discloses thixotropic coating compositions prepared from a binder and a sag control agent which is the reaction product of a diisocyanate and a monoamine or hydroxy monoamine. Similarly, EP-A-0 261 863 discloses fluidity controlling agents for paints which give thixotropic properties to a coating film when it is applied to the paint and hardly produces sagging in the formation of thick coating films.

15

However, the performance of conventional sagging agents is not always sufficient and fairly high amounts of sagging agents may be necessary to get the desired sag control. Accordingly, there is a need for sag control agents with an improved performance so that the amount that is to be used can be reduced and/or the  
20 tendency of sagging is further reduced. Furthermore there is a need for sag control agents that give completely clear and transparent clear coats in both 1K and 2K systems.

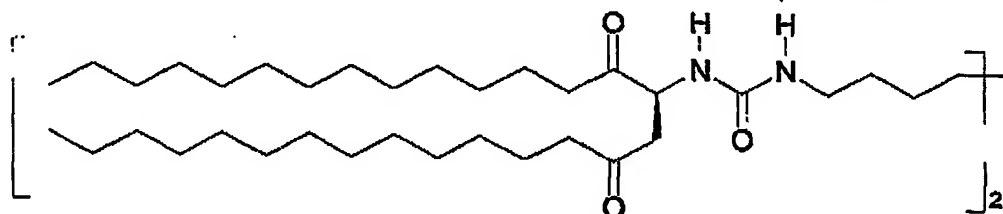
Surprisingly, we found that a specific class of urea compounds is able to deliver  
25 the performance that is needed.

Accordingly, the present invention relates to an optically active urea, obtainable by reacting one or more isocyanates with one or more optically active, carbon-

ANR 3011 PD EP

2

substituted, methyl amines of the formula 
$$\begin{array}{c} R^1 \\ | \\ R^2 - C^* - NH_2 \\ | \\ R^3 \end{array}$$
, wherein each of  $R^1$ ,  $R^2$ , and  $R^3$  are independently selected from hydrogen, linear or branched, substituted or unsubstituted hydrocarbyl, including substituted or unsubstituted phenyl or naphthyl, whereby each of  $R^1$ ,  $R^2$ , and  $R^3$  is different such that the carbon atom is a chiral centre, with the proviso that the amine is not an amino acid, not an amino acid ester, and not a compound of the formula



The latter compound is described by L.A. Estroff and A.D. Hamilton in Angew. Chem. Int. Ed. 2000, 39, No.19, p3447-3450 to be an effective gelator for water. The invention also relates to the use of such a urea as a sagging controlling agent (SCA).

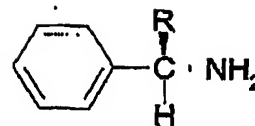
Preferably R is linear or branched, substituted or unsubstituted  $C_1$ - $C_{25}$  alkyl. More preferably R is linear or branched  $C_1$ - $C_{25}$  alkyl. Even more preferably R is linear or branched  $C_1$ - $C_{10}$  alkyl. If present, the substituents are preferably selected from the group consisting of alkyl, alkoxy, hydroxy, amine, carboxylic acid, phosphonic acid, keto, ketimine, amino, urethane, allophanate, urea, and isocyanurate groups. Preferably the amine is not optically pure 1,2-diaminecyclohexane.

In a first preferred embodiment the SCA according to the invention is obtained by reacting an isocyanate with at least one optically active substituted benzyl amine

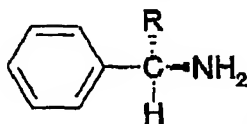
ANR 3011 PD EP

3

selected from compounds of the formulae



I) and



II), wherein R is a linear or branched, substituted or

unsubstituted hydrocarbyl. If present, the substituents are preferably selected from the group consisting of hydroxy, amine, carboxylic acid, phosphonic acid, keto,

5 ketimine, amino, ether, urethane, allophanate, urea, and isocyanurate groups. Preferably R is linear or branched, substituted or unsubstituted  $C_1$ - $C_{25}$  alkyl. More preferably R is linear or branched  $C_1$ - $C_{25}$  alkyl. Even more preferably R is linear or branched  $C_1$ - $C_5$  alkyl. Most preferably R is a methyl or ethyl group.

- 10 Any suitable isocyanate may be used for the preparation of a sag control agent according to the invention, such as an aliphatic or araliphatic or cycloaliphatic or aromatic diisocyanate. Preferably a diisocyanate or a polyisocyanate with, on average, more than two isocyanate per molecule is used. Most preferably, a diisocyanate is used. The diisocyanate usually contains 3 to 40, and preferably 4
- 15 to 20 carbon atoms. It is preferred that use is made of a symmetrical aliphatic or cycloaliphatic diisocyanate. As suitable examples of diisocyanates may be mentioned tetramethylene-1,4-diisocyanate, hexamethylene-1,6-diisocyanate (HMDI), .omega.,.omega.- dipropylether diisocyanate, thiodipropyl diisocyanate, cyclohexyl-1,4- diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, 1,5-
- 20 dimethyl(2,4-.omega.-diisocyanato methyl) benzene, 1,5-dimethyl(2,4-.omega.-diisocyanatoethyl) benzene, 1,3,5-trimethyl(2,4-.omega.- diisocyanatomethyl) benzene, 1,3,5-triethyl(2,4-.omega.- diisocyanatomethyl) benzene, the trimer of

ANR 3011 PD EP

4

hexamethylene-1,6-diisocyanate (HMDI) and other polyisocyanates based on HMDI, including isocyanurates, biurets, an asymmetrical trimer, etc. , many of which are marketed as Desmodur® N and Tolonate® HDB and HDT, isophoron diisocyanate, dicyclohexyldimethylmethane-4,4'- diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate and diphenylmethane-4,4'-diisocyanate (MDI). Hexamethylene-1,6-diisocyanate, and an aromatic diisocyanate, for instance: toluene diisocyanate are preferred. Preferred poly-isocyanates are known as "polymeric MDI" and are typically a mixture of pure MDI and oligomers of MDI. Also carbodiimide modified isocyanates can be used. Most preferably HMDI is used to make SCAs according to the invention.

As will be understood by the person skilled in the art, one can also use conventionally blocked isocyanates which generate one or more isocyanates in situ, as long as the blocking agent, after splitting, does not prevent the formation of the SCA according to the invention.

Throughout this document the term "isocyanate" is used to denominate all of the isocyanates and isocyanate-generating compounds.

In the reaction between the isocyanate and the amine for the preparation of the sag control agent either the isocyanate or the amine may generally be employed in excess relative to the stoichiometric amount. For example, the ratio of the number of amino groups of the amine to the number of (generated) isocyanate groups may be in the range of 0.7 to 1.5. Preferably, however, the ratio is about 1.

It is to be understood that any mixture of stable chiral amines of formulae I) and II) can be used to make an SCA to the invention, as long as this mixture is optically

ANR 3011 PD EP

5

active. However, it is preferred to use as little as possible a mixture of enantiomers with opposite optical activity, since it was observed that racemic mixtures have only conventional activity as an SCA, whereas the use of just one enantiomers resulted in an SCA with improved properties.

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Furthermore, it is to be noted that the SCA that is formed will also be optically active. When a preferred diisocyanate is used, the final SCA may be in the d-, l-, and/or meso- form. Since one enantiomers of the amine will be in excess, also the resulting SCA will contain an excess of the d- or l- form and, therefore, be optically  
10 active. The resulting optically active SCAs were found to have the desired benefits.

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The reaction between the isocyanate and the amine may generally be carried out in any arbitrarily chosen way by combining the reaction components, optionally at elevated temperature. It is preferred that the reaction should be carried out in an  
15 atmosphere of an inert gas at temperatures in the range of 0 to 150 °C., more particularly in the range of 20 to 80 °C. Although in general the reaction components may be combined in any arbitrarily chosen manner, it is as a rule preferred that the isocyanate should be added to the amine, which may be done in several steps, if desired. Generally, the reaction is carried out in the presence of  
20 an inert organic solvent, such as for example, acetone, methyl isobutyl ketone, N-methyl pyrrolidone, benzene, toluene, xylene, or an aliphatic hydrocarbon such as petroleum ether, but the use of a solvent is optional. If so desired also other compounds which can be used in a final coating composition can be used as a solvent or dispersing medium in the preparation step of the SCA, provided that this  
25 solvent or dispersing medium does not prevent the formation of the SCA. For instance, a polymer polyol can be used for such a purpose. If such an inert

ANR 3011 PD EP

6

dispersion medium is used, it may not be necessary to disperse the SCA in another liquid component of the final coating composition as described hereinafter.

The preparation of the sag control agent may optionally also be carried out in the presence of a binder. It is preferred then that a mixture of the binder and the isocyanate should be mixed with a mixture of the binder and the amine. The mixing operation may be carried out in any convenient manner, with the reactants being vigorously stirred. In a preferred embodiment of this method the binder is mixed with such amounts of the isocyanate and the amine that upon conclusion of the reaction there is obtained a mixture to be used as master batch of the sag control agent, consisting of 5-70, preferably 6-50, more preferably 7-25, parts by weight of the sag control agent relative to 95-30, preferably 94-50, more preferably 93-75, parts by weight of the binder. Optionally further diluents or adjuvants may be present. Preferably, the concentrate contains 5-70%, preferably 6-50%, more preferably 7-25% by weight of the sag control agent. However, the SCA may also be produced in the binder or curing component of the final coating formulation, in such a low concentration that the binder can be subsequently used in the coating composition without that further binder or curing component and/or SCA needs to be added. In a most preferred embodiment the SCA according to the invention is prepared in the binder at the desired concentration, so that the mixing-in of concentrates is not necessary.

If a concentrate of the SCA is desired, a preferred mixture consists of 5-70, preferably 6-50, more preferably 7-25, parts by weight of the sag control agent relative to 95-30, preferably 94-50, more preferably 93-75, parts by weight of the

ANR 3011 PD EP

7

- binder. Optionally the concentrate can comprise further diluents or adjuvants. Products with more than 30% by weight of the SCA generally are in the form of a powdered or crumbled mixture which can very readily be homogeneously mixed with the binder to be employed in the preparation of the thixotropic coating composition. Preferably, the concentrate contains 5-70%, preferably 6-50%, more preferably 7-25% by weight of the sag control agent. The binders in the thixotropic coating composition and in the master batch of the sag control agents may be of the same or of different composition. Particularly, if the binder need be present in the master batch in only a small amount, the respective binders may chemically differ. The preferred concentrates are suitably prepared in an atmosphere of inert gas at a temperature in the range of 20 to 80 °C, with the amine first being added to a binder material and, after the mixture has been homogenized, the isocyanate being slowly added to the mixture, with stirring.
- 15 Although less desired, one can also prepare binder or curing compositions comprising the sag control agent by preparing said binder or curing compounds in the presence of said sag control agent or by preparing the binder or curing compound as well as the sag control agent at the same time. The skilled person will have no problem in combining the SCA, or starting materials for an SCA, with
- 20 the starting materials for the binder or curing compound with subsequent reaction to form the SCA-containing binder or curing compositions.

If the sag control agent is not prepared in the binder or curing compound, it can be mixed with one or more of the components of the coating composition, preferably

25 the binder or any other liquid component, as a result of which preferably a

ANR 3011 PD EP

8

homogeneous mixture is obtained. The mixtures of the preferred embodiment typically form a dispersion of the SCA in the liquid component, such as the binder or an inert diluent. When used to formulate coating compositions, the resulting coating composition with improved rheology, here dubbed thixotropic, may have  
5 an opaque, an opalescent or even a transparent appearance, depending on the size and the refractive index of the dispersed particles of the sag control agent.

The degree to which the rheology of the coating composition is changed depends, Inter alia, on the proportion of sag control agent and the nature of the sag control  
10 agent and the components of the coating composition. As a rule, the desired degree of thixotropy may be obtained by employing the sag control agent in an amount of 0.01 to 30 percent and preferably 0.1 to 10 percent by weight, based on the total amount of coating composition.

15 The thixotropic coating compositions according to the invention may contain polar and/or non-polar solvents if such solvents do not adversely influence the thixotropic character. Preferably, the thixotropy is present not only at room temperature, but also at elevated temperature, so that the sag control agent according to the invention is suitable for use at room temperature and in baking  
20 paints, which are usually cured at temperatures in the range of 60 to 250 °C.

The sag control agents according to the invention are particularly suitable for use in coating compositions having a high solids content, because they seldom or not at all increase the viscosity of the coating composition, so that no solvent or only a

ANR 3011 PD EP

9

- very small amount thereof is needed to bring the coating composition in an applicable state. By a coating composition having a high solids content is to be understood here a composition having a solids content of at least 70 percent by weight. The solids content is determined in accordance with the ASTM Method D 1644-59 with heating for 1 hour at 105 °C. The sag control agent according to the invention further has the considerable advantage that it does not or seldom decreases the gloss of the composition, particularly if the composition contains a pigment.
- 10 Depending on the binder and curing system that is employed, any conventional compound can be used as binder and curing agent. However, since the SCAs were found to be particularly suited to improve the rheology in conventional two component (2-K) coating systems. In such 2-K systems there is typically one component, either binder or curing agent, having one or more pendant groups as presented in Table I, while the second component comprises one or more co-reactive groups as listed in Table I.

ANR 3011 PD EP

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Table I

Pendant functional group	Co-reactive groups
Carboxylic acid (anhydride)	Oxirane, carbodlimide, aziridine, azetidine, oxazoline, hydroxyl, amino, carboxylic acid
Oxirane/epoxy	Carboxylic acid (anhydride), amino, thiol, hydroxyl, oxirane
Hydroxy	Methylol, etherified methylol, isocyanate, aldehyde
Acetoacetoxyl	Amino, aldehyde, isocyanate, methylol, ketimine
Amino	Acetoacetoxyl, oxirane, aldehyde, ketone, isocyanate, carbamate
Ketone	Amino, hydrazide
Aldehyde	Amino, hydrazide
Isocyanate	Hydroxy, amino, thiol
Thiol	isocyanate, thiol, oxirane
Alkoxysilane	carboxylic acid (anhydride), hydroxyl, water
Carbamate	amino, etherified methylol
activated unsaturated groups (e.g. (meth)acryloyl)	acetoacetate, malonate, thiol, amino
cyclic carbamate	amino, carboxylic acid (anhydride), hydroxyl
Oxazoline	Carboxylic acid (anhydride)

- Preferably, the binder-curing system preferably is a 2-K coating system. More preferably, the 2-K coating system is based on hydroxy-isocyanate, epoxy-amine, epoxy-acid or anhydride, or ketimine-acetoacetate systems. The coating composition may further contain usual adjuvants and additives, for instance pigment dispersants, dyes, pigments, solvents and accelerators for the curing reaction, for instance acidic compounds such as p-toluene sulphonic acid or blocked products thereof.

ANR 3011 PD EP

11

The thixotropic coating compositions may be applied to a substrate in any desired manner, for instance by rolling, spraying, brushing, sprinkling, casting, dipping or electrostatic spraying.


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The thixotropic coating composition may further be cured or baked in the usual way, for instance at ambient temperatures or in an oven at the usual temperatures, for instance in the range of 80 to 250 °C., over a period of 2 to 120 minutes.

10 The invention is elucidated by the following examples.

### Experimental

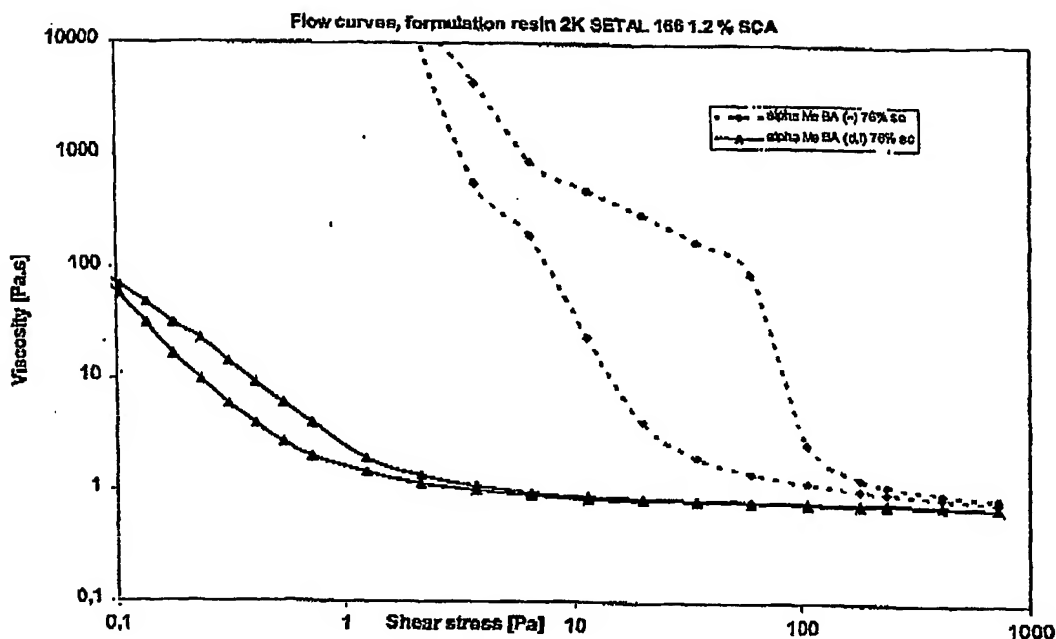
#### Examples 1 and Comparative Examples A

15 1-Phenyl 1-amino ethane (or methylbenzylamine, abbreviated alphaMe BA) was prepared in a conventional way. The product can be obtained from BASF as R-PEA (ChiPros® (R)-(+)-1-Phenylethylamin) and/or S+PEA (ChiPros® (S)-(-)-1-Phenylethylamin). Both 1.73g of a racemic mixture and the S-enantiomer of alphaMe BA was mixed in 100g Setal® 166 SS 80 (80% in butyl acetate), a  
20 polyester polyol ex Akzo Nobel suitable for use in 2K coating applications, and subsequently reacted with 1.21g hexylene-1,6-diisocyanate at 20°C. The reaction product was diluted with further Setal® 166 SS 80 (80% in butyl acetate), to obtain a product with 1.2 parts by weight of SCA, based on 100 parts by weight of the polyester polyol. The rheological data is presented in the following flow curve.

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ANR 3011 PD EP

12



Clearly, the optical active enantiomer gives much higher viscosity at low shear, while giving a comparable viscosity at high shear stresses.

5

The optically active enantiomer was found to be a very good sag control agent in a conventional 2K isocyanate system based on this material which resulted in a fully transparent cured film. The SCA based on the racemic mixture of amines was less effective in controlling the sagging of the uncured coating film and comparable to the sagging of a conventional SCA. In the same 2K coating system conventional sag control agents are known to give a cured film with a slight haze.

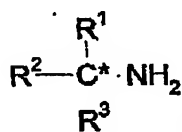
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ANR 3011 PD EP

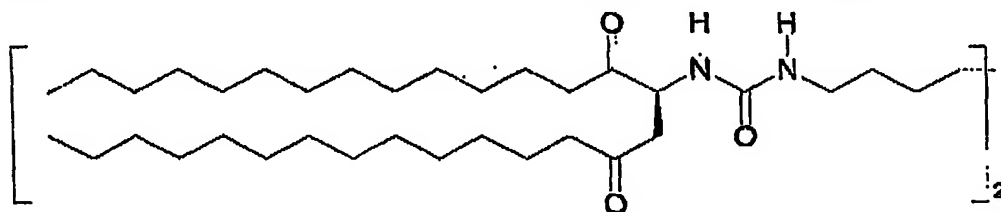
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CLAIMS

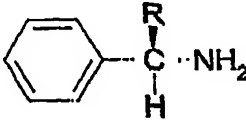
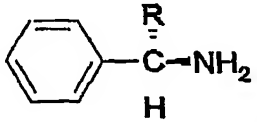
- 5 1. A sag control agent obtainable by reacting one or more isocyanates with at least one optically active carbon-substituted methylamine of the formula



- wherein each of R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are independently selected from hydrogen and linear or branched, substituted or unsubstituted hydrocarbyl, whereby each of R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> is different such that the carbon atom is a chiral centre, with the proviso that the amine is not an amino acid, not an amino acid ester, and not a compound of the formula



2. A sag control agent according to claim 1 wherein the amine is selected from

- 15 compounds of the formulae  I) and  II), wherein R is a linear or branched, substituted or unsubstituted hydrocarbyl.

ANR 3011 PD EP

14

3. A sag control agent according to claim 2 wherein R is linear or branched, substituted or unsubstituted C<sub>1</sub>-C<sub>25</sub> alkyl, preferably a linear or branched C<sub>1</sub>-C<sub>25</sub> alkyl, even more preferably a linear or branched C<sub>1</sub>-C<sub>5</sub> alkyl, most preferably a methyl or ethyl group.

5

4. Concentrates of a sag control agent according to any one of claims 1-3 in a binder or inert diluent.

5. Compositions with improved rheology comprising a sag control agent according to any one of claims 1-3.

10

6. Composition according to claim 5 which is a coating or adhesive composition.

7. Use of a sag control agent according to any one of claims 1-3 in coating compositions to reduce the tendency of sagging of a coating film, obtained by applying said coating composition onto a substrate, before said coating film is cured.

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ANR 3011 PD EP

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**Abstract**

The invention relates to sag control agents that are obtainable by reacting an optically active substituted methyl amine, other than an amino acid, and an  
5 isocyanate. Also the use of such sag control agents to change the rheology of a composition, particularly a coating composition.